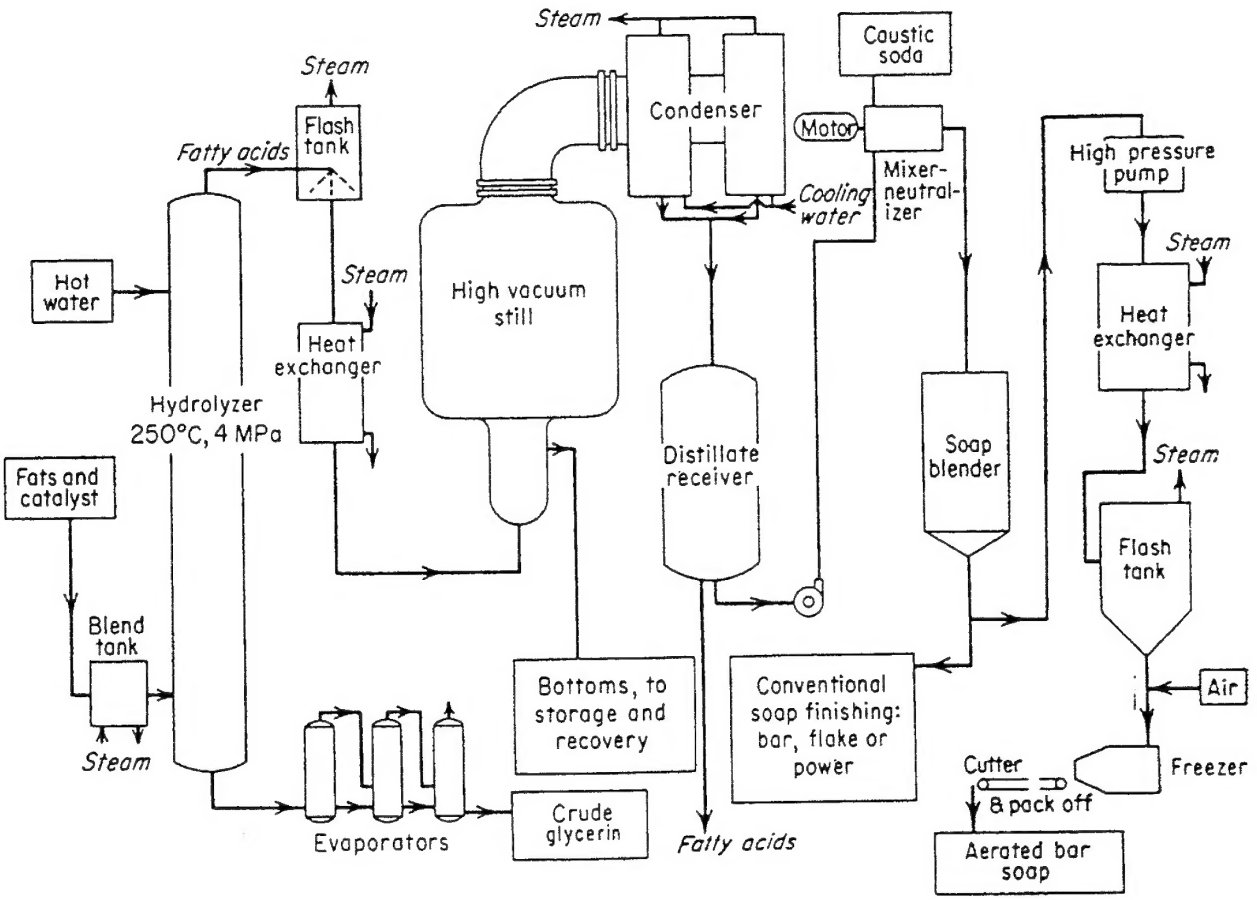


Fig. 3.3. Continuous process for the production of fatty acids and soap. *(Procter & Gamble Co.)*

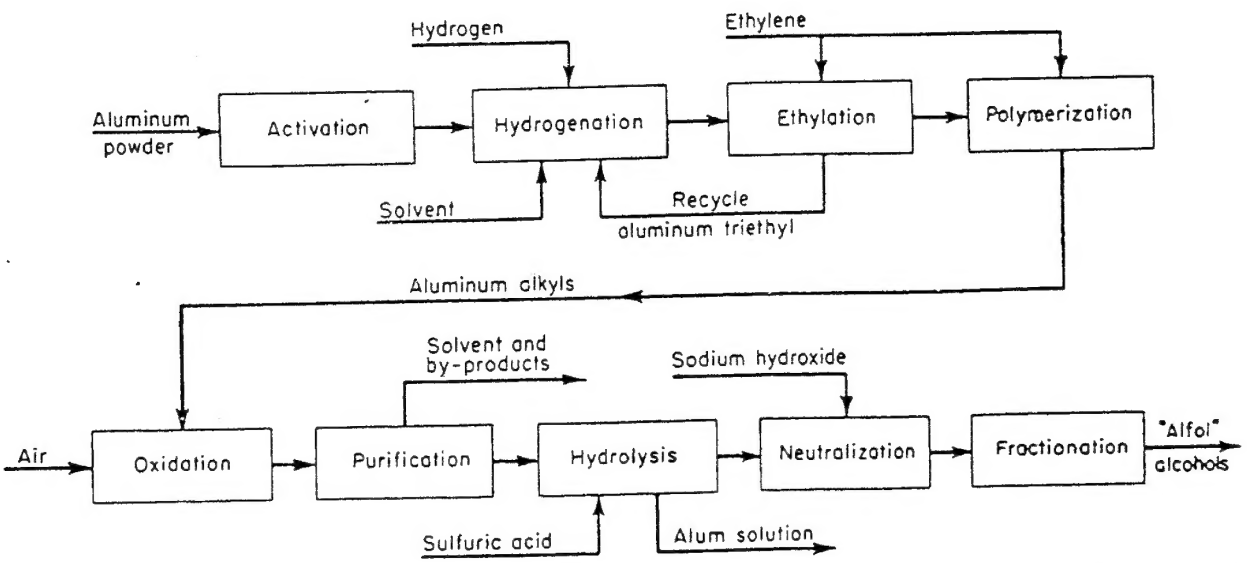
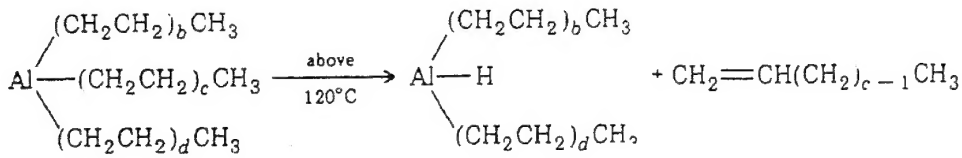


Fig. 3.4. The alfol process. Fatty alcohols made by means of the organometallic route have carbon chain lengths ranging from 6 to 20 carbons. The alfol process used by Conoco commences by reacting aluminum metal, hydrogen, and ethylene, all under high pressure, to produce *aluminum triethyl*. This compound is then polymerized with ethylene to form aluminum alkyls. These are oxidized with air to form aluminum alkoxides. Following purification, the alkoxides are hydrolyzed with 23 to 26% sulfuric acid to produce crude, primary, straight-chain alcohols. These are neutralized with caustic, washed with water, and separated by fractionation. Basic patents covering the process have been licensed. *(DuPont-Conoco.)*

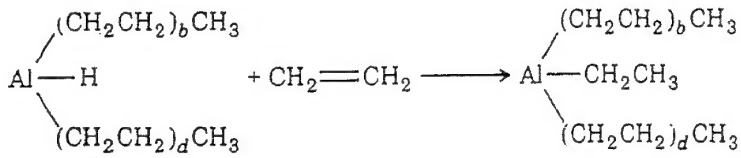
Each ethyl group on the aluminum triethyl can add ethylene to form aluminum trialkyls of 4 to 16 or more carbons per alkyl group.

DISPLACEMENT REACTIONS

Thermal decomposition

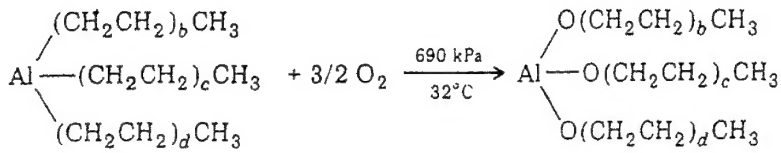


Regeneration of ethyl group



The growth and displacement reactions take place concurrently, but the thermal decomposition reaction is much slower than the regeneration reaction and thus is the rate-determining step for the overall reactions. These reactions take place repeatedly as long as unreacted ethylene is present. They are run in an inert hydrocarbon solvent such as heptane or benzene. In these solvents aluminum "trialkyl" is not pyrophoric at less than 40% concentration. It takes approximately 140 min to build up to a C_{12} average chain length when reacting 5 mol of ethylene for each ⅓ mol of aluminum triethyl The trialkyl aluminum is oxidized to yield an aluminum trialkoxide, which in turn is treated with sulfuric acid to give alkyl or fatty alcohols.

OXIDATION REACTION



ΔH is exothermic, liberating about 2.5 MJ/kg of oxidized alkyl. Its conversion is 98 percent at 32°C in about 2 h.

HYDROLYSIS (ACIDOLYSIS)

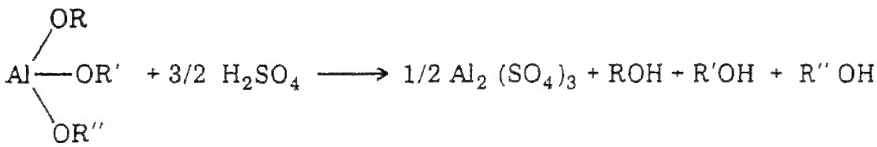


Figure 3.4 gives a flow diagram of the production of alcohols using these reactions.

Fatty Alcohols from Methyl Esters. Fats have long been basic raw materials for soaps and detergents. Such fats as are available are glyceryl esters of fatty acids (C_6 to C_{24}) and

have been hydrolyzed to the acids for soaps and reduced to the alcohols by catalytic hydro genation for detergents. The methyl esters of fatty acids[12] are also hydrogenated to fatt alcohols. These esters are prepared by reacting methanol with coconut or tallow triglyceride catalyzed by a small amount of sodium methylate. The refined oil is first dried by flashing a 150°C under a vacuum of 16.6 kPa, as otherwise it will consume relatively expensive sodiun methylate and also form soap. The methyl exchange esterification takes place in about a hour; then the reaction mix is settled and separated into an upper layer rich in ester an methanol and a lower layer rich in glycerin and methanol. The ester layer is washed coun tercurrently to remove excess methanol, to recover glycerin, and to remove the catalyst which would poison the hydrogenation. Yields of fatty alcohols are 90 to 95 percent.

Hydrogenation of methyl esters is catalyzed by a complex catalyst of copper II and coppe III chromite (made from copper nitrate, chromic oxide, and ammonia, with final roasting and is carried out at approximately 21 MPag and 260 to 315°C. The continuous equipmen used is outlined in Fig. 3.5 and consists of three vertical reactors 12 m high using 30 mol o heated hydrogen per mole of ester; the hydrogen serves not only for reducing but also fo heating and agitation. The crude alcohols are fractionated to the specified chain length.

SUDS REGULATORS. Suds regulation is often necessary for surfactants to do an efficient jo of cleaning in a washing machine. This is often achieved by combining different types suc as anionics with nonionics, or anionics with soap. For soaps, foam inhibition increases wit the amount of saturation and the number of carbons in the fatty acid residue. Soaps of satu rated C_{20-24} fatty acids are good foam inhibitors.[13] Other foam inhibitors are higher fatty acic

[12]ECT, 3d ed., vol. 1, 1978, p. 732.

[13]Sittig, op cit., p. 446.

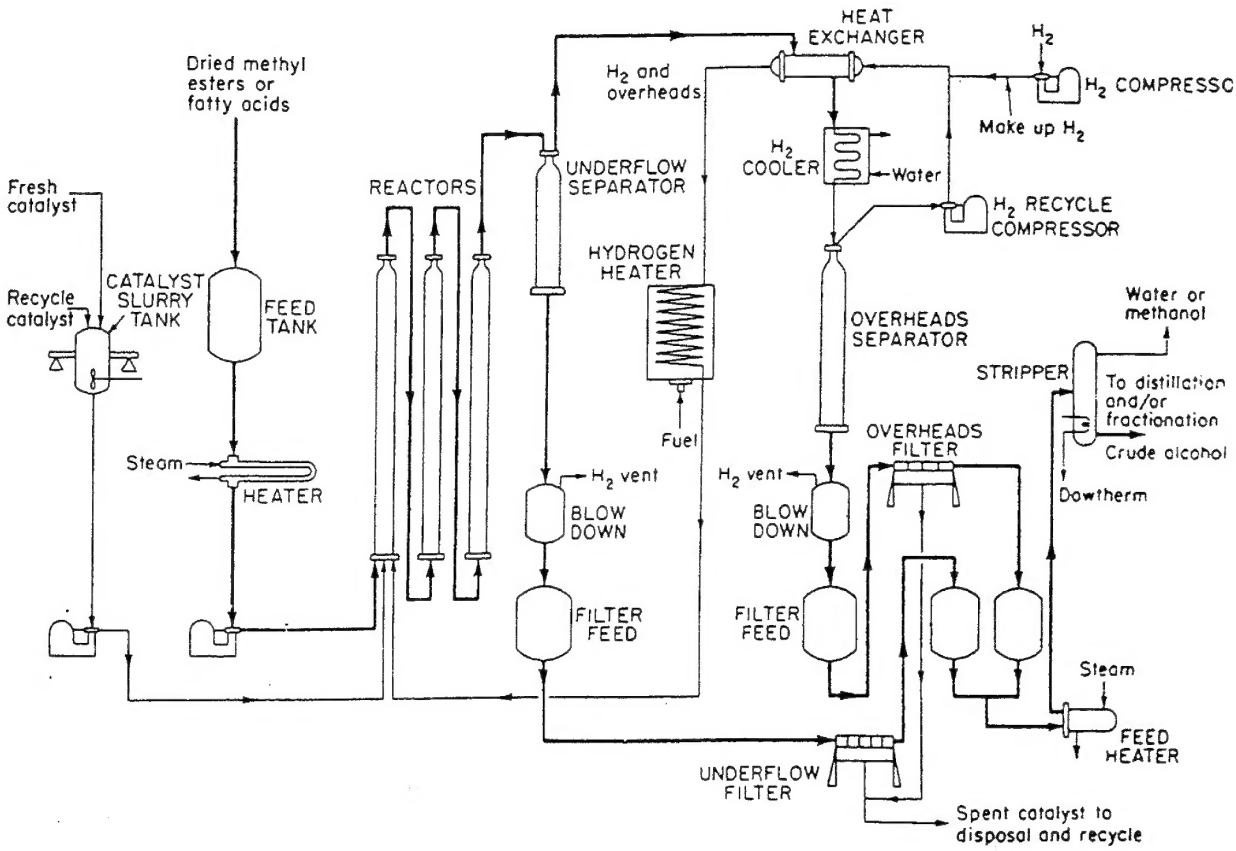


Fig. 3.5. Flowchart for the hydrogenolysis of methyl esters to obtain fatty alcohols and glycerin from natural fats. *(ECT, 3d ed., vol. 4, 1978, p. 837.)*

amides, aliphatic carboxylic acid esters containing at least 18 carbons in one or preferably both acid and alcohol chains, and *N*-alkylated aminotriazines.

BUILDERS. Builders boost detergent power. Complex phosphates, such as sodium tripolyphosphate, have been used most extensively. These are more than water softeners which sequester water-hardening calcium and magnesium ions. They prevent redeposition of soil from the wash water on fabrics. Proper formulation with complex phosphates has been the key to good cleaning with surfactants and made possible the tremendous development of detergents. Polyphosphates (e.g., sodium tripolyphosphate and tetrasodium pyrophosphate) have a synergistic action with the surfactant together with an enhanced effectiveness and hence reduce the overall cost. The rapid rise in the acceptance of detergents stemmed from the building action of the polyphosphates. During the 1960s the growth of algae and eutrophication in lakes became linked to the presence of phosphates in detergents. Several states restricted phosphate use so that substitutes had to be found. The first compound suggested was nitrilotriacetic acid (NTA), but it was declared a carcinogen in 1970. But new research results have vindicated its safety; in 1980 the EPA said it saw no reason to regulate NTA. This has not freed NTA for use because various congressional and environmental groups have challenged the EPA decision. There are no restrictions on its use in Canada.

Other builders are citrates, carbonates, and silicates. The newest, and seemingly most promising, substitute for phosphates is the use of zeolites.[14] By 1982 about 136 kt/year of zeolites were being used as detergent builders. The builder market is large and amounts to over 1000 kt annually. In 1980 phosphates accounted for 50 percent, zeolites 12 percent, silicates 13 percent, carbonates 12 percent, and NTA and citrates 2 percent each.

ADDITIVES. *Corrosion* inhibitors, such as sodium silicate, protect metal and washer parts, utensils, and dishes from the action of detergents and water. Carboxymethyl cellulose has been used as an *antiredeposition* agent. *Tarnish inhibitors* carry on the work of the corrosion inhibitor and extend protection to metals such as German silver. Benzotriazole has been used for this purpose. *Fabric brighteners* are fluorescent dyes which make fabrics look brighter because of their ability to convert ultraviolet light to visible light. Two dyes thus used are 4(2H-naphtho[1,2-d]triazol-2-yl)stilbene-2-sulfonate and disodium 4,4′-bis(4-anilino-6-morpholino-*S*-triazin-2-ylamino)-2,2′-stilbene disulfonate.

Bluings improve the whiteness of fabrics by counteracting the natural yellowing tendency. The ingredients used for this purpose can vary from the long-used ultramarine blue (bluing) to new dye materials. *Antimicrobial* agents include carbanilides, salicylanilides, and cationics. Peroxygen-type *bleaches* are also employed in laundry products. The use of *enzyme*-containing detergents has been common in Europe for several years and recently has been introduced into the United States. The enzymes decompose or alter the composition of soil and render the particles more easily removable. They are particularly useful in removing stains, particularly those of a protein nature.

Manufacture of Detergents

Table 31.5 compares three types of detergents. The most widely used detergent, a heavy-duty granule, is presented in Fig. 29.6, with the quantities of materials required. The reactions are:

[14]Layman, Detergents Shift Focus of Zeolites Market, *Chem. Eng. News* 60 (39) 10 (1982).

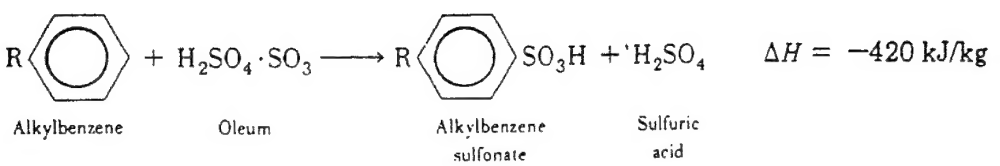
***Table* 3.5** Basic Composition of Three Types of Dry Phosphate-Based Detergents (Granules)

Ingredient	Function	Ingredient on Dry-Solids Basis, wt %		
		Light-Duty High Sudsers	Heavy-Duty Controlled Sudsers	Heavy-Duty High Sudsers
Surfactants				
Organic active, with suds regulators	Removal of oily soil, cleaning	25–40	8–20	20–35
Builders				
Sodium tripolyphosphate and/or tetrasodium pyrophosphate	Removal of inorganic soil, detergent-building	2–30	30–50	30–50
Sodium sulfate	Filler with building action in soft water	30–70	0–30	10–20
Soda ash	Filler with some building action	0	0–20	0–5
Additives				
Sodium silicate having 2.0 $\leq SiO_2/Na_2O \leq 3.2$	Corrosion inhibitor with slight building action	0–4	6–9	4–8
Carboxymethyl cellulose	Antiredeposition of soil	0–0.5	0.5–1.3	0.5–1.3
Fluorescent dye	Optical brightening	0–0.05	0.05–0.1	~0.1
Tarnish inhibitors	Prevention of silverware tarnish	0	0–0.02	0–0.02
Perfume and sometimes dye or pigment	Aesthetic, improved product characteristics	0.1	0.1	0.1
Water	Filler and binder	1–5	2–10	3–10

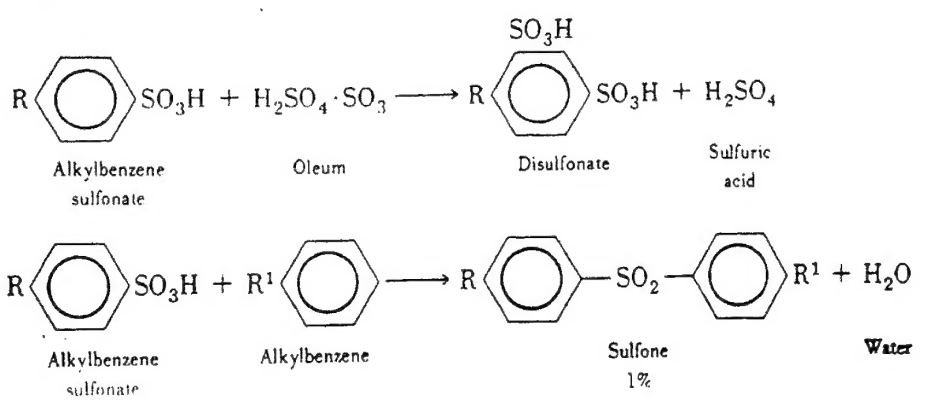
SOURCE: Van Wazer, *Phosphorus and Its Compounds*, vol. 2, Interscience, New York, 1961, p. 1760.

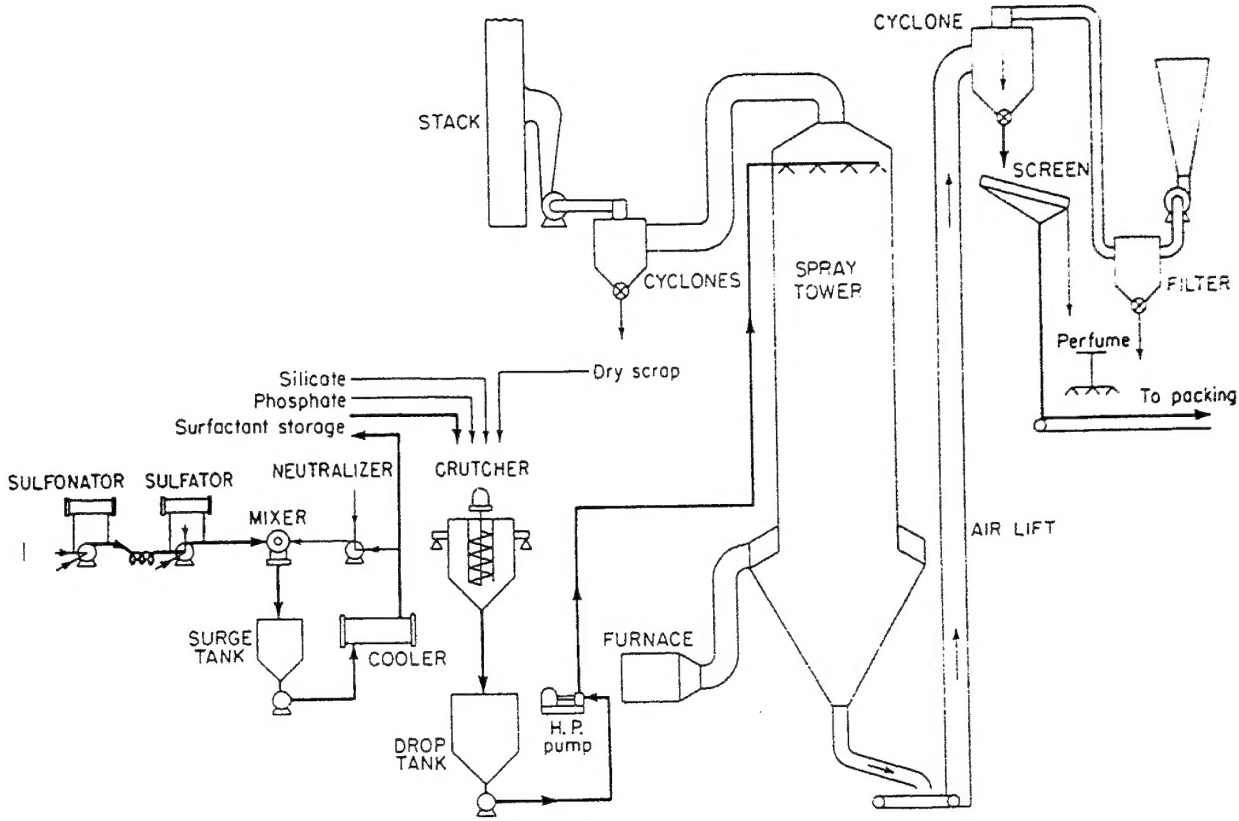
LINEAR ALKYLBENZENE SULFONATION

1. Main reaction:



2. Secondary reactions:





In order to produce 1 t of finished product, the following materials (in kilograms) are required:

Surfactant Materials		Corrosion Inhibitor	
Alkylbenzene (petrochemical)	75	Sodium silicate	125
Fatty alcohol (from tallow)	75	Builder	
Oleum	150	Sodium tripolyphosphate	500
NaOH solution	200	Miscellaneous additives	30
		Water	500

Fig. 3.6. Simplified continuous flowchart for the production of heavy-duty detergent granules. *(Procter & Gamble Co.)*

FATTY ALCOHOL SULFATION

1. Main reaction:

$$R{-}CH_2OH + SO_3 \cdot H_2O \rightleftharpoons R'OSO_3H + H_2O \qquad \Delta H = -325 \text{ to } -350 \text{ kJ/kg}$$

2. Secondary reactions:

$$R{-}CH_2OH + R'{-}CH_2{-}OSO_3H \rightarrow R{-}CH_2{-}O{-}CH_2{-}R' + H_2SO_4$$
$$R'{-}CH_2{-}CH_2OH + SO_3 \rightarrow R'{-}CH{=}CH_2 + H_2SO_4$$
$$R{-}CH_2OH + SO_3 \rightarrow RCHO + H_2O + SO_2$$
$$R{-}CH_2OH + 2SO_3 \rightarrow RCOOH + H_2O + 2SO_2$$

This presentation is supplemented by Table 3.5, which gives the basic constituents in more detail for the three types of detergent granules. The continuous flowchart in Fig. 3.6 can be broken down into the following coordinated sequences:

Sulfonation-sulfation. The alkylbenzene (AB) is introduced continuously into the sulfonator with the requisite amount of oleum, using the dominant bath principle shown in Fig. 29.8 to control the heat of sulfonation conversion and maintain the temperature at about 55°C. Into the sulfonated mixture is fed the fatty tallow alcohol and more of the oleum. All are pumped through the sulfater, also operating on the dominant bath principle, to maintain the temperature at 50 to 55°C, thus manufacturing a mixture of surfactants.

Neutralization. The sulfonated-sulfated product is neutralized with NaOH solution under controlled temperature to maintain fluidity of the surfactant slurry. The surfactant slurry is conducted to storage.

The surfactant slurry, the sodium tripolyphosphate, and most of the miscellaneous additives are introduced into the crutcher. A considerable amount of the water is removed, and the paste is thickened by the tripolyphosphate hydration reaction:

$$\underset{\text{Sodium tripolyphosphate}}{Na_5P_3O_{10}} + 6H_2O \longrightarrow \underset{\text{Sodium tripolyphosphate hexahydrate}}{Na_5P_3O_{10}\cdot 6H_2O}$$

This mixture is pumped to an upper story, where it is *sprayed* under high pressure into the 24-m-high spray tower, counter to hot air from the furnace. Dried granules of acceptable shape and size and suitable density are formed. The dried granules are transferred to an upper story again by an air lift which cools them from 115°C and stabilizes the granules. The granules are separated in a cyclone, screened, perfumed, and packed.

The sulfonation conversion is shown in Fig. 3.7 to be extremely fast. The reactions also need to have the high heats of reaction kept under control, as shown in more detail in Fig. 29.8, depicting the circulating heat exchanger, or dominant baths, for both these chemical conversions and for neutralization. The use of oleum in both cases reduces the sodium sulfate in the finished product. However, the oleum increases the importance of control to prevent oversulfonation. In particular, alkylbenzene sulfonation is irreversible and results in about 96 percent conversion in less than a minute when run at 55°C with 1 to 4% excess SO_3 in the oleum. A certain minimum concentration of SO_3 in the oleum is necessary before the sulfonation reaction will start, which in this case is about 78.5% SO_3 (equivalent to 96% sulfuric acid). As both these reactions are highly exothermic and rapid, efficient heat removal is required to prevent oversulfonation and darkening. Agitation is provided by a centrifugal pump, to which the oleum is admitted. The recirculation ratio (volume of recirculating material divided by the volume of throughput) is at least 20:1 to give a favorable system. To provide the sulfonation time to reach the desired high conversion, more time is allowed by conducting the mixture through a coil, where time is given for the sulfonation reaction to go to completion.

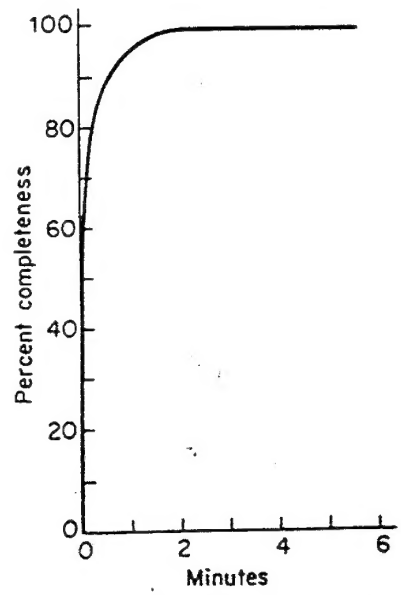


Fig. 3.7. Alkylbenzene sulfonation completeness versus time at 55°C. *(Procter & Gamble Co.)*

Neutralization of the acid slurry releases six to eight times as much heat as the sulfonation reaction. Here a

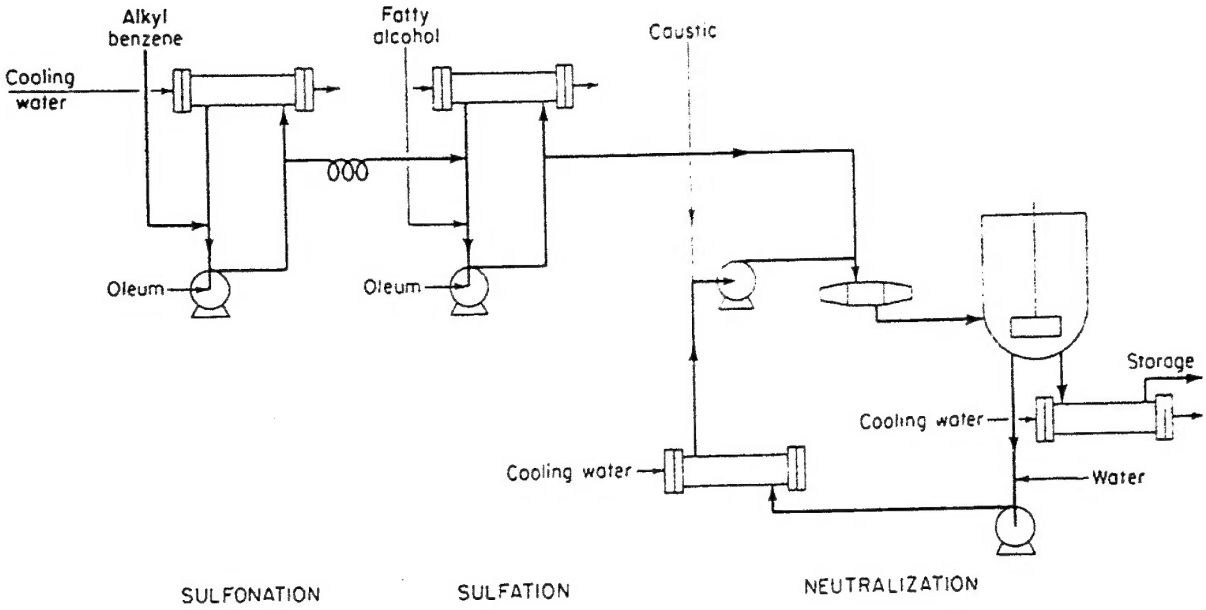


Fig. 3.8. Continuous series sulfonation-sulfation, ending with neutralization, in the circulating heat-exchanging dominant bath to control heat. *(Procter & Gamble Co.)*

dominant bath (Fig. 3.8) is employed which quickly effects the neutralization, since a partly neutralized acid mix is very viscous.

SOAP

Soap comprises the sodium or potassium salts of various fatty acids, but chiefly of oleic, stearic, palmitic, lauric, and myristic acids. For generations its use has increased until its manufacture has become an industry essential to the comfort and health of civilized human beings. The relative and overall production of soap and detergents is shown by the curve in Fig. 3.1. History and industrial statistics are discussed in the first part of this chapter (Table 3.1).

Raw Materials

Tallow is the principal fatty material in soapmaking; the quantities used represent about three-fourths of the total oils and fats consumed by the soap industry, as shown in Fig. 3.1. It contains the mixed glycerides obtained from the solid fat of cattle by steam rendering. This solid fat is digested with steam; the tallow forms a layer above the water, so that it can easily be removed. Tallow is usually mixed with coconut oil in the soap kettle or hydrolyzer in order to increase the solubility of the soap. Greases (about 20 percent) are the second most important raw material in soapmaking. They are obtained from hogs and smaller domestic animals and are an important source of glycerides of fatty acids. They are refined by steam rendering or by solvent extraction and are seldom used without being blended with other fats. In some

cases, they are treated so as to free their fatty acids, which are used in soap instead of the grease itself. Coconut oil has long been important. The soap from coconut oil is firm and lathers well. It contains large proportions of the very desirable glycerides of lauric and myristic acids. Free fatty acids are utilized in soap, detergent, cosmetic, paint, textile, and many other industries. The acidification of "foots," or stock resulting from alkaline refining of oils, also produces fatty acids. The important general methods of splitting are outlined in Table 3.4. The Twitchell process is the oldest.[15] Continuous countercurrent processes are now most commonly used.

The soapmaker is also a large consumer of chemicals, especially caustic soda, salt, soda ash, and caustic potash, as well as sodium silicate, sodium bicarbonate, and trisodium phosphate. Inorganic chemicals added to the soap are the so-called builders. Important work by Harris of Monsanto and his coworkers[16] demonstrated conclusively that, in particular, tetrasodium pyrophosphate and sodium tripolyphosphate were unusually effective synergistic soap builders. Of considerable economic importance was the demonstration that combinations of inexpensive builders, such as soda ash, with the more effective (and expensive) tetrasodium pyrophosphate or sodium tripolyphosphate, were sometimes superior to the phosphate used alone. It was further shown that less soap could be used in these mixtures to attain the same or more effective soil removal.

Manufacture

The manufacture of soap is presented in Fig. 3.3. The long-established kettle[17] process, however, is mainly used by smaller factories or for special and limited production. As soap technology changed, continuous alkaline saponification was introduced. Computer control allows an automated plant for continuous saponification by NaOH of oils and fats to produce in 2 h the same amount of soap (more than 300 t/day) made in 2 to 5 days by traditional batch methods.

The present procedure involves continuous splitting, or hydrolysis, as outlined in Table 3.2 and detailed in Fig. 3.3. After separation of the glycerin, the fatty acids are neutralized to soap.

The basic chemical reaction in the making of soap is saponification.[18]

$$\underset{\text{Caustic soda}}{3NaOH} + \underset{\text{Glyceryl stearate}}{(C_{17}H_{35}COO)_3C_3H_5} \rightarrow \underset{\text{Sodium stearate}}{3C_{17}H_{35}COONa} + \underset{\text{Glycerin}}{C_3H_5(OH)_3}$$

[15]This process is described in more detail in CPI 2, p. 619.

[16]*Oil Soap* 19 3 (1942); Cobbs et al., *Oil Soap* 17 4 (1940); Wan Wazer, "Phosphorus and Its Compounds," chap. 27, in *Detergent Building*, Interscience, New York, 1958.

[17]Full descriptions with flowcharts for the kettle process full-boiled (several days), semi-boiled, and cold are available on pp. 623–625 of CPI 2.

[18]Although stearic acid is written in these reactions, oleic, lauric, or other constituent acids of the fats could be substituted. See Table 28.1 for fatty acid composition of various fats and oils.

The procedure is to split, or hydrolyze, the fat, and then, after separation from the valuable glycerin, to neutralize the fatty acids with a caustic soda solution:

$$\underset{\text{Glyceryl stearate}}{(C_{17}H_{35}COO)_3C_3H_5} + 3H_2O \rightarrow \underset{\text{Stearic acid}}{3C_{17}H_{35}COOH} + \underset{\text{Glycerin}}{C_3H_5(OH)_3}$$

$$\underset{\text{Stearic acid}}{C_{17}H_{35}COOH} + \underset{\text{Caustic soda}}{NaOH} \rightarrow \underset{\text{Sodium stearate}}{C_{17}H_{35}COONa} + H_2O$$

The usual fats and oils of commerce are not composed of the glyceride of any one fatty acid, but of a mixture. However, some individual fatty acids of 90% purity or better are available from special processing. Since the solubility and hardness of the sodium salts (Table 3.6) of the various fatty acids differ considerably, the soapmaker chooses the raw material according to the properties desired, with due consideration of the market price.

In continuous, countercurrent splitting the fatty oil is deaerated under a vacuum to prevent darkening by oxidation during processing. It is charged at a controlled rate to the bottom of the hydrolyzing tower through a sparge ring, which breaks the fat into droplets. These towers, about 20 m high and 60 cm in diameter, are built of Type 316 stainless steel (see Fig. 3.5). The oil in the bottom contacting section rises because of its lower density and extracts the small amount of fatty material dissolved in the aqueous glycerin phase. At the same time daerated, demineralized water is fed to the top contacting section, where it extracts the glycerin dissolved in the fatty phase. After leaving the contacting sections, the two streams enter the reaction zone.[19] Here they are brought to reaction temperature by the direct injection of high-pressure steam, and then the final phases of splitting occur. The fatty acids are discharged from the top of the splitter or hydrolyzer to a decanter, where the entrained water is separated or flashed off. The glycerin-water solution is then discharged from the bottom of an automatic interface controller to a settling tank. See Fig. 3.10 for glycerin processing.

Although the crude mixtures of fatty acids resulting from any of the above methods may be used as such, usually a separation into more useful components is made. The composition of the fatty acids from the splitter depends upon the fat or oil from which they were derived.

[19]Allen et al., Continuous Hydrolysis of Fats, *Chem. Eng. Prog.*, 43 459 (1947); Fatty Acids, *Chem. Eng.* 57 (11), 118 (1950); Ladyn, Fat Splitting, *Chem. Eng.* 71 (17) 106 (1964) (continuous flowcharts).

***Table* 3.6** Solubilities of Various Pure Soaps (in grams per 100 g of water at 25°C)

	Stearate	Oleate	Palmitate	Laurate
Sodium	0.1*	18.1	0.8*	2.75
Potassium	—	25.0	—	70.0*
Calcium	0.004†	0.04	0.003	0.004†
Magnesium	0.004	0.024	0.008	0.007
Aluminum	*i*	*i*	*d*	

*Approximate.
†Solubility given at 15°C only.
NOTE: *i* indicates that the compound is insoluble; *d* indicates decomposition.

Those most commonly used for fatty acid production include beef tallow and coconut, palm, cottonseed, and soybean oil. Probably the most used of the older processes is panning and pressing. This fractional crystallization process is limited to those fatty acid mixtures which solidify readily, such as tallow fatty acid. The molten fatty acid is run into pans, chilled, wrapped in burlap bags, and pressed. This expression extracts the liquid red oil (mainly oleic acid), leaving the solid stearic acid. The total number of pressings indicates the purity of the product. To separate fatty acids of different chain lengths, distillation[20] is employed, vacuum distillation being the most widely used. Three fractionating towers of the conventional tray type are operated under a vacuum. Preheated, crude fatty acid stock is charged to the top of a stripping tower. While it is flowing downward, the air, moisture, and low-boiling fatty acids are swept out of the top of the tank. The condensate, with part of it redrawn as a reflux, passes into the main fractionating tower, where a high vacuum is maintained at the top. A liquid side stream, also near the top, removes the main cut (low-boiling acids), while overheads and noncondensables are withdrawn. The liquid condensate (high-boiling acids) is pumped to a final flash tower, where the overhead distillate is condensed and represents the second fatty acid fraction. The bottoms are returned to the stripping tower, reworked, and removed as pitch. The fatty acids may be sold as such or converted into many new chemicals.

The energy requirements that enter into the cost of producing soap are relatively unimportant in comparison with the cost of raw materials, packaging, and distribution. The energy required to transport some fats and oils to the soap factory is occasionally considerable. The reaction that goes on in the soap reactor is exothermic.

The following are the principal sequences into which the making of bar soap by water splitting and neutralization can be divided, as shown by the flowchart in Fig. 3.3.

Transportation of fats and oils.

Transportation and manufacture of caustic soda.

Blending of the catalyst, zinc oxide, with melted fats and heating with steam takes place in the blend tank.

Hot melted fats and catalysts are introduced into the bottom of the hydrolyzer.

Splitting of fats takes place countercurrently in the hydrolyzer at 250°C and 4.1 MPa, continuously, the fat globules rising against a descending aqueous phase.

The aqueous phase, having dissolved the split glycerin (about 12%), falls and is separated.

The glycerin water phase is evaporated and purified. See Glycerin.

The fatty acids phase at the top of the hydrolyzer is dried by flashing off the water and further heated.

In a high-vacuum still the fatty acids are distilled from the bottoms and rectified.

The soap is formed by continuous neutralization with 50% caustic soda in high-speed mixer-neutralizer.

The neat soap is discharged at 93°C into a slowly agitated blending tank to even out any inequalities of neutralization. At this point the neat soap analyzes: 0.002 to 0.10% NaOH, 0.3 to 0.6% NaCl, and approximately 30% H_2O. This neat soap may be extruded, milled, flaked, or spray-dried, depending upon the product desired. The flowchart in Fig. 29.3 depicts the finishing operations for floating bar soap.

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[20]Fatty Acid Distillation, *Chem. Eng.* 55 146 (1948). Pictured flowcharts of both straight and fractional distillation; Marsel and Allen, Fatty Acid Processing, *Chem. Eng.* 54 (6) 104 (1947); ECT, 3d ed., vol. 4, 1978, p. 839.

These finishing operations are detailed: The pressure on the neat soap is raised to 3.5 MPa, and the soap is heated to about 200°C in a high-pressure steam exchanger. This heated soap is released to a flash tank at atmospheric pressure, where a partial drying (to about 20%) takes place because the soap solution is well above its boiling point at atmospheric pressure. This viscous, pasty soap is mixed with the desired amount of air in a mechanical scraped-wall heat exchanger, where the soap is also cooled by brine circulation in the outer shell from 105°C to about 65°C. At this temperature the soap is continuously extruded in strip form and is cut into bar lengths. Further cooling, stamping, and wrapping complete the operation. This entire procedure requires only 6 h, as compared with over a week for the kettle process. The main advantages of soap manufactured by this process as compared with the kettle process are (1) improved soap color from a crude fat without extensive pretreatment, (2) improved glycerin recovery, (3) flexibility in control, and (4) less space and labor. Intimate molecular control is the key to the success of this continuous process, as, for example, in the hydrolyzer, where the desired mutual solubility of the different phases is attained by appropriate process conditions.

Typical Soaps

The main classes of soap are toilet soaps and industrial soaps. These different soaps can frequently be made by one or more of the procedures described. The bar soap[21] market consists of regular and superfatted toilet soaps, deodorant and/or antimicrobial soaps, floating soaps, transparent/translucent, marbelized, and hard water soaps. Some overlapping occurs as some deodorant bars have a superfatted base. Toilet soap is usually made from mixtures of tallow and coconut oil in ratios of 80/20 or 90/10, and superfatted soaps have ratios of 50/50 or 60/40 and some have 7 to 10% free fatty acid added as well. Deodorant soaps contain an agent such as 3,4′,5-tribromosalicylanilide (TBS) which prevents the decomposition of perspiration into odorous compounds.

Practically all soap merchandised contains from 10 to about 30% water. If soap were anhydrous, it would be too hard to dissolve easily. See Table 3.6. Almost all soaps contain perfume, even though it is not apparent, serving merely to disguise the original soapy odor. Toilet soaps are made from selected materials and usually contain only 10 to 15% moisture; they have very little added material, except for perfume and perhaps a fraction of a percent of titanium dioxide as a whitening agent. Shaving soaps contain a considerable proportion of potassium soap and an excess of stearic acid, the combination giving a slower-drying lather. "Brushless" shaving creams contain stearic acid and fats with much less soap.

Another type of bar soap (in comparison with the floating type in Fig. 3.3) is milled toilet soap. The word milled refers to the fact that, during processing, the soap goes through several sets of heavy rolls, or mills, which mix and knead it. Because of the milling operation, the finished soap lathers better and has a generally improved performance, especially in cool water. The milling operation is also the way in which fragrant perfumes are incorporated into cold soap. If perfume were mixed with warm soap, many of the volatile scents would evaporate. After the milling operation, the soap is pressed into a smooth cylinder and is extruded continuously. It is then cut into bars, stamped, and wrapped as depicted in Fig. 3.9.

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[21]Jungerman, New Trends in Bar Soap Technology, *Soap Cosmet. Chem. Spec.* 58 (1) 31 (1982).

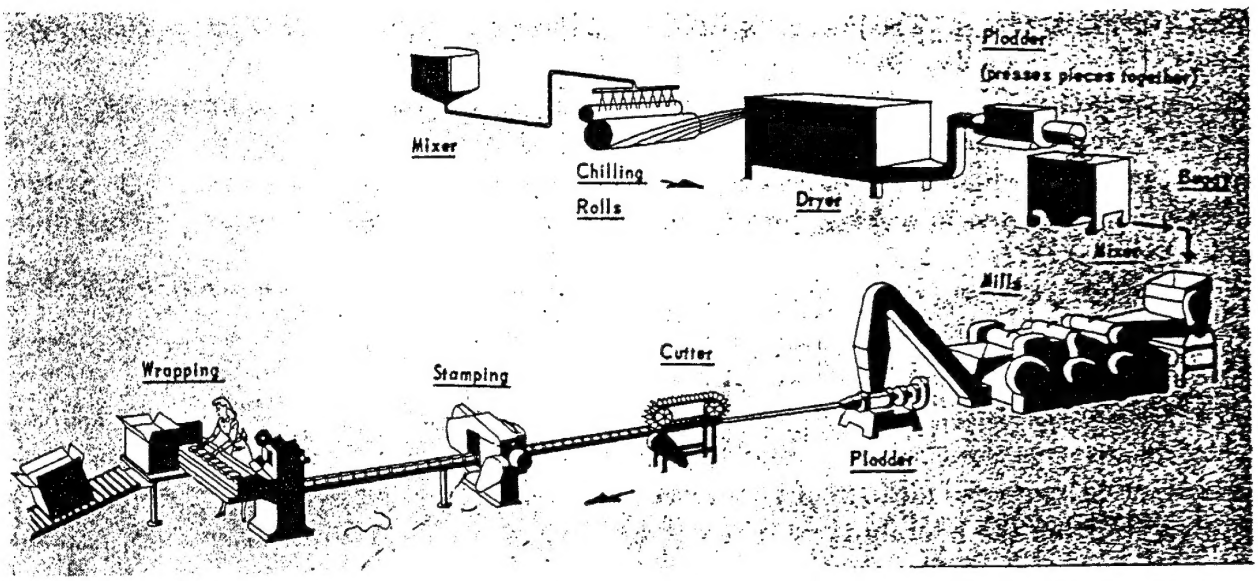

Fig. 3.9. Making soap in milled bars. Another type of bar soap (in comparison with the floating type shown in Fig. 3.3) is milled toilet soap. The word "milled" refers to the fact that, during processing, the soap goes through several sets of heavy rolls or mills which mix and knead it. A much more uniform product is obtained, and much direct labor is saved.

Crystal Phases in Bar Soap. The physical properties of bar soap are dependent upon the crystalline soap phases present and the condition of these phases. Any of three or more phases may exist in sodium soaps, depending upon the fat used, the moisture and electrolyte composition of the system, and the processing conditions. Milled toilet soaps are mechanically worked to transform the omega phase, at least partially, to the translucent beta phase producing a harder, more readily soluble bar. Extruded floating soaps contain both crystals formed in the freezer and crystals that grow from the melt after it leaves the freezer. Processing conditions are adjusted for an optimum proportion of crystallized matrix, which adds strength and rigidity to the bar. If necessary, the bar may be tempered by reheating to strengthen it.

GLYCERIN

HISTORICAL. Glycerin[22] is a clear, nearly colorless liquid having a sweet taste but no odor. Scheele first prepared glycerin in 1779 by heating a mixture of olive oil and litharge. On washing with water, a sweet solution was obtained, giving, on evaporation of the water, a viscous heavy liquid, which the discoverer called "the sweet principle of fats." In 1846 Sobrero produced the explosive nitroglycerin for the first time, and in 1868 Nobel, by absorbing it in kieselguhr, made it safe to handle as dynamite. These discoveries increased the demand for glycerin. This was in part satisfied by the development in 1870 of a method for recovering glycerin and salt from spent soap lyes. Since about 1948, glycerol has been produced from petrochemical raw materials by synthetic processes.

[22]The term *glycerin* is chosen for the technical product containing the pure trihydroxy alcohol *glycerol*. The spelling of glycerin is that employed by the USP.

USES AND ECONOMICS. The production of crude glycerin is approximately 150 kt/year. Synthetic glycerin furnishes about 40 percent of the market. Glycerin is supplied in several grades, including USP and CP, grades which are chemically pure, contain not less than 95% glycerol, and are suitable for resins and other industrial products. Yellow distilled is used for certain processes where higher-purity types are not essential, e.g., as a lubricant in tire molds. Glycerin is employed in making, preserving, softening, and moistening a great many products, as shown in Table 3.7.

Manufacture

Glycerin may be produced by a number of different methods, of which the following are important: (1) the saponification of glycerides (oils and fats) to produce soap, (2) the recovery of glycerin from the hydrolysis, or splitting, of fats and oils to produce fatty acids, and (3) the chlorination and hydrolysis of propylene and other reactions from petrochemical hydrocarbons.

In recovering glycerin from soap plants, the energy requirements are mostly concerned with heat consumption involved in the unit operations of evaporation and distillation, as can be seen by the steam requirements on the flowchart in Fig. 29.10. The breakdown of natural and synthetic procedures for glycerin is:

Glycerin from Sweet Water from Hydrolyzer	Glycerin from Petroleum
Evaporation (multiple effect) for concentration	Purification of propylene
Purification with settling	Chlorination to allyl chloride
Steam vacuum distillation	Purification and distillation
Partial condensation	Chlorination with HOCl
Decoloration (bleaching)	Hydrolysis to glycerin
Filtration or ion-exchange purification	Distillation

RECOVERY FROM FATTY ACIDS. Practically all natural glycerin is now produced as a coproduct of the direct hydrolysis of triglycerides from natural fats and oils. Hydrolysis is

Table 3.7 Glycerin Consumption (metric kilotons)

	1978	1980
Alkyd resins	21.5	27
Cellophane	6.4	8
Tobacco	14.2	25
Explosives	2.9	3
Drugs and cosmetics	24.1	38
Urethane foams	13.8	18
Foods and beverages	14.8	24
Miscellaneous	15.8	16

SOURCE: ECT, 3d ed., vol. 11, 1980, p. 927; *Chem. Mar. Rep*, May 25, 1981.

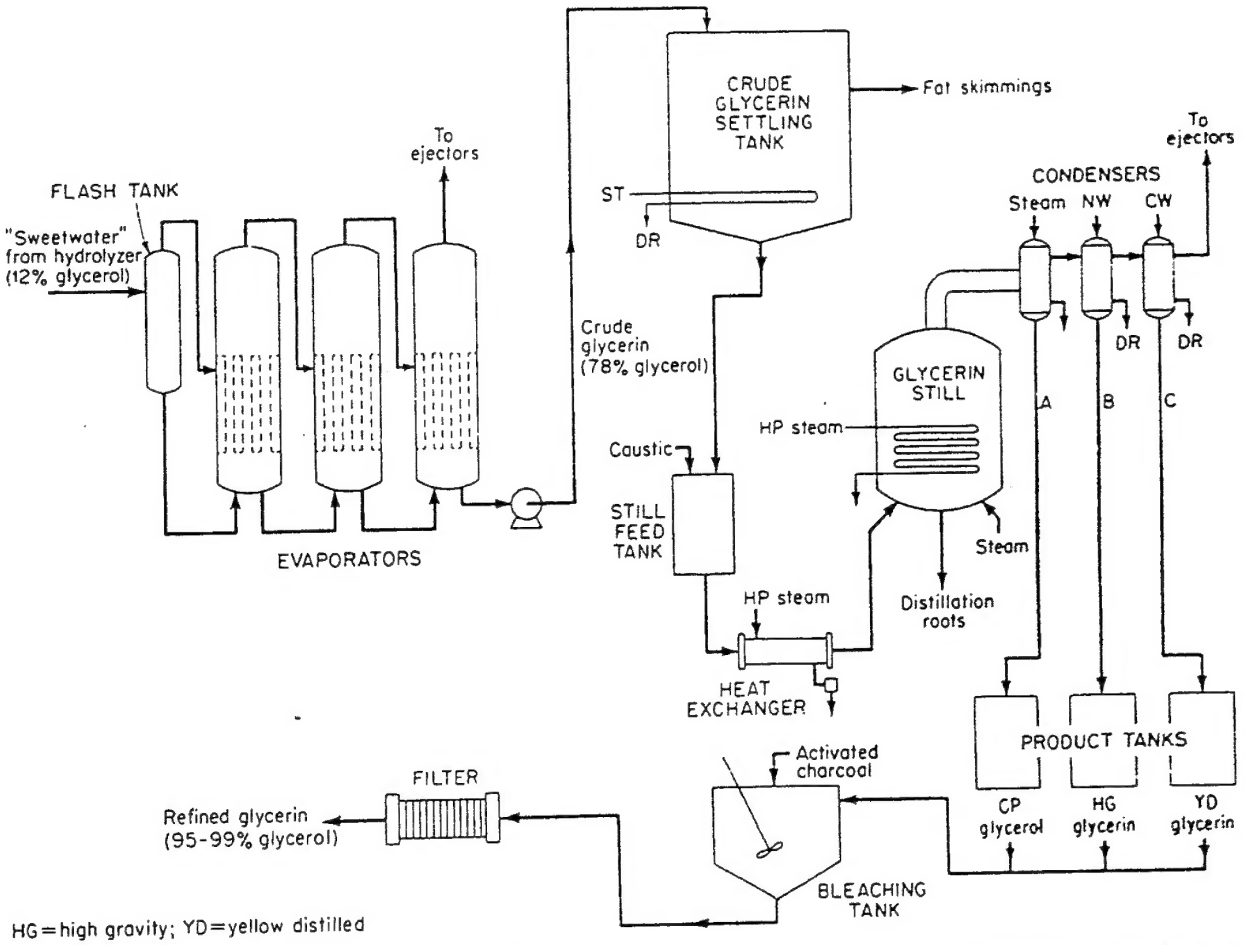

Fig. 3.10. Flowchart for glycerin manufacture from hydrolysis of sweet water *(Procter & Gamble Co.)*

carried out in large continuous reactors at elevated temperatures and pressures with a catalyst. Water flows countercurrent to the fatty acid and extracts glycerol from the fatty phase. The sweet water from the hydrolyzer column contains about 12% glycerol. Evaporation of the sweet water from the hydrolyzer is a much easier operation compared with evaporation of spent soap lye glycerin in the kettle process. The high salt content of soap lye glycerin requires frequent soap removal from the evaporators. Hydrolyzer glycerin contains practically no salt and is readily concentrated. The sweet water is fed to a triple-effect evaporator, as depicted by the flowchart in Fig. 3.10, where the concentration is increased from 12% to 75 to 80% glycerol. Usually, no additional heat (other than that present in the sweet-water effluent from the hydrolyzer) is required to accomplish the evaporation. After concentration of the sweet water to hydrolyzer crude, the crude is settled for 48 h at elevated temperatures to reduce fatty impurities that could interfere with subsequent processing. Settled hydrolyzer crude contains approximately 78% glycerol, 0.2% total fatty acids, and 22% water. The settled crude is distilled under a vacuum (8 kPa) at approximately 200°C. A small amount of caustic is usually added to the still feed to saponify fatty impurities and reduce the possibility of codistillation with the glycerol. The distilled glycerin is condensed in three stages at decreasing temperatures. The first stage yields the purest glycerin, usually 99% glycerol, meeting CP specifications. Lower-quality grades of glycerin are collected in the second and third condensers. Final purification of glycerin is accomplished by carbon bleaching, followed by filtration or ion exchange.